# Soluble multiferroic hybrids

Polyakov, Alexey

# Chapter 1. Introduction

This chapter gives a general introduction to the hybrid materials described in this thesis. First the general structure of layer- and chain-type hybrids is described and the overview of the synthesis method is presented. Then the magnetic interactions in the inorganic part of 1D and 2D hybrids are discussed. Section 2 of the present chapter is dedicated to the specific phenomena discussed later in the corresponding chapters.

The general idea of the work of this thesis is to demonstrate that the robust properties of the organic-inorganic hybrids like ferroelectricity and magnetism can be tuned with the assistance of the organic moieties. The structural flexibility of the hybrids implies the possibility of substitution of the organic ligands in order to tune the inorganic component which defines the properties. Moreover, the interface between the organic and inorganic parts creates remarkable opportunities, like ferroelectricity in $CuCl_4$-based hybrids, discussed in Chapter 3.

## 1.1 Layer- and chain-type organic-inorganic hybrids

Layered crystal structures are present in a rich variety of materials with properties including topological insulators, superconductivity[1,2], ferroelectricty[3] and colossal magnetoresistance[4]. One of the most interesting and promising classes in this family situates itself at the boundary between the perovskite materials and metal-organic frameworks (MOFs): organic-inorganic hybrids[5–11]. They combine the robust functional properties of the inorganic perovskite with the structurally versatile organization of MOFs, creating a remarkable merger. Extensive study over the last years revealed that these organic-inorganic hybrids exhibit ferromagnetism[12–14], photovoltaic properties[15,16] and multiferroicity[17–22].

Hybrids, discussed in this thesis generally consist of alternating ordered inorganic and organic parts, where the $NH_3$ group provides the organic-inorganic connectivity. I am going to focus on two types of such an organic-inorganic hybrids: layer-type and chain-type (hereafter 2D and 1D hybrids), named in correspondence to the dimensionality of the inorganic part.

### 1.1.1 General structure of 1D and 2D hybrids

As mentioned, hybrids consist of ordered organic and inorganic parts. Hybrid materials benefit from the nature of both parts: robust magnetic and electronic properties from the inorganic part as well as easy-processing and structural flexibility from the organic moiety. The hybrids have three atomic "building blocks" which form the structure of the material, namely- metal ion, halogen and organic ligand. Variation of these blocks provides a possibility to achieve hybrids with defined dimensionality and properties. The inorganic part is defined by the metal ion and its order defines the overall dimensionality of the hybrid.

In case of $Cu^{2+}$, $Mn^{2+}$ and $Fe^{2+}$ the inorganic part represents perovskite-like layers of $MX_6$ (where M=Cu, Mn, Fe and X=Cl, Br) corner-shared octahedra[14,23,24]. These layers are separated by ordered double layers of the organic ligands, placed tail-to-tail in the neighboring layers (Fig 1). For the hybrids discussed in this thesis organic ligands with general formula $Y\mathit{NH_3}$ were used (where $Y=C_nH_{n+2}$,$C_6H_5C_2H_2$, etc.). The connectivity between the organic and inorganic part is provided by hydrogen bond ordering via $NH_3$ to halogen connections. The representation of the structure of 2D hybrid with general formula $MX_4(Y\mathit{NH_3})_2$ is shown in Figure 1.1.

In one-dimensional hybrids (where $M=Ni^{2+}$) organic-inorganic connectivity remains the same, while the structure of the inorganic part is different. $MX_6$ octahedra connect to each via face-sharing in case of $M= Ni^{2+}$. Such an arrangement of the octahedra forms inorganic chains (Fig. 1.2). In 1D hybrids the inorganic chain also form layers, and chains in the layer are connected via the $NH_3$ groups of the organic ligands.

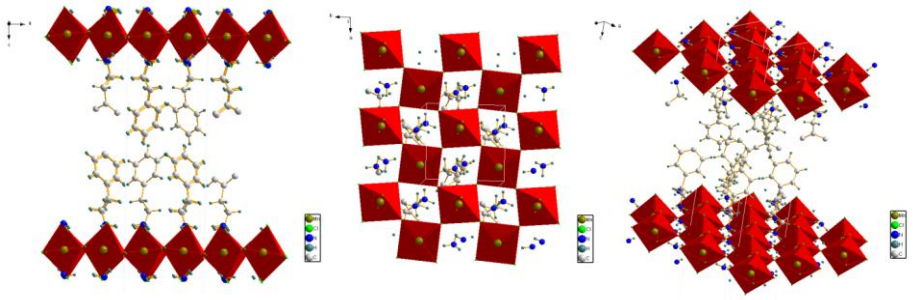

**Figure 1.1**. Representation of the crystal structure of the 2-dimensional $MnCl_4$-based hybrids in different crystallographic orientations, along the b-axis (left), along the c-axis (middle) and slightly tilted from the b-axis (right).

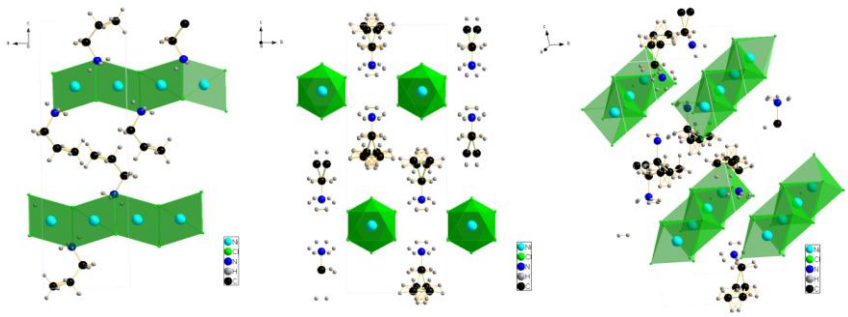

**Figure 1.2**. Representation of crystal structure of the 1 dimensional $NiCl_3$-based hybrid in different orientations: along the b-axis (left), along the a-axis (middle), tilted from the [1,1,1] axis.

### 1.1.2 Synthesis techniques

Synthesis techniques for 1D and 2D hybrids are the same, due to a similar formation of the backbone of the hybrid- $MX_6$ inorganic octahedra. D. Mitzi demonstrated a variety of techniques for the deposition of hybrids[5,7]. Generally, hybrids can be synthesized as a bulk or film. In order to grow

single crystals of the hybrids, a solution growth method was used. With this method it was possible to grow large single crystals for structural, magnetic and electronic transport measurements. From my experience, solution growth is one of the most convenient methods to grow single crystals of hybrids with a certain range of flexibility of the end product parameters. For example, controlling the growth parameters, like temperature and atmosphere, thickness, size and homogeneity of the end product can be controlled. Moreover, some hybrids need special conditions during the synthesis and the growth, e.g. closed atmosphere or particular temperature. This method is described in details in Chapter 2.

In this thesis most of the organic-inorganic hybrids were synthesized as single crystals by the solution method. However, to synthesize hybrid thin films with the possibility to control thickness down to the nanometer scale the Langmuir-Blodgett technique was used[25,26], described in Chapter 5.

Among others the most prominent one appears to be the spin-coating technique[5,6,27], which was used to create a Sn-based hybrid thin film transistor[28]. In this technique a saturated solution of the pre-made hybrid compound is spread (coated) over the spinning substrate. The advantage of this method is the ability to control the thickness of the deposited sample. However, the spin coating technique does not offer the control of homogeneity of the coverage and quality of the sample. Besides spin-coating, the dipping technique attracts significant interest, due to its simple deposition procedure[29,30]. First, a metallic salt is evaporated on the substrate using vacuum evaporation methods. Then, this substrate is dipped into the saturated organic salt solution, thus forming single layer of the hybrid. After that, the procedure can be continued to reach the desired number of layers. Another promising method is double source thermal ablation technique[31]. Similar to PLD[32], in this method organic and inorganic precursors are stored in two different heating baths in a vacuum chamber, in front of which a substrate is fixed. While the baths are heated, precursors precipitate on the substrate, thus, forming the hybrid compound. As discovered by C. Stoumpos et al. in his work on Sn-based hybrids, the synthesis technique slightly influences the properties of the hybrids[33].

### 1.1.3 Magnetic interactions in the inorganic part of 1D and 2D hybrids

In the organic-inorganic hybrids magnetism originates from the transition metal ions in the inorganic perovskite-like sheets[12]. In the case of two-dimensional hybrids inorganic sheets are formed by the corner-shared octahedra $MX_6$ (M- metal, X- halogen). In this case neighboring ions interact in-plane antiferromagnetically via a nearly $180^o$ superexchange path through the halogen ions, situated between the metal ions[24,34]. It is important that non Jahn-Teller active magnetic ions exhibit antiferromagnetic interactions in-plane. Good examples of such a magnetic behavior are the Mn- and Fe-based hybrids. Superexchange interactions are possible via M-X-M $180^0$ pathways (Fig.1.3). Also, usually magnetic spins of these hybrids are not aligned perpendicular to the inorganic plane, but exhibit canting. Therefore, a small ferromagnetic moment is present. A ferromagnetic interlayer coupling causes 3D order.

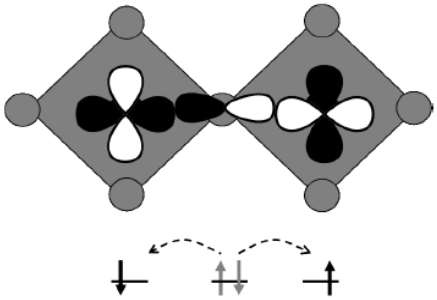

**Figure 1.3**. The magnetic superexchange interaction between two magnetic ions in the inorganic plane of the 2D hybrid.

However, in the case of Jahn-Teller active ions like $Cr^{2+}$ or $Cu^{2+}$-based hybrids, alternation of long and short bonds due to Jahn-Teller effect leads to a specific orbital arrangement similar to $K_2CuF_4$[35](Fig. 1.4). The magnetic spin is located in the $d_{x^2-y^2}$ orbital, which aligns with the long axis of the octahedron. Thus, the orbitals on neighboring metal ions are orthogonal to each other and the spins experience ferromagnetic superexchange via a

180° M-X-M pathway.[21] The ferromagnetic coupling leads to in-plane 2D order and an apparent quasi 3D ferromagnetic ordering.

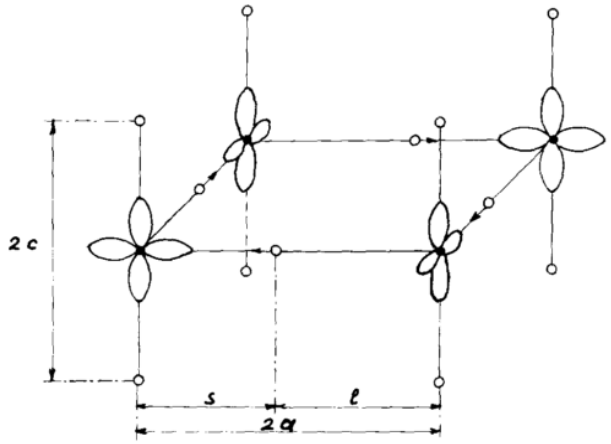


**Figure 1.4**. The orbitals shown on the structure of the basal plane in $K_2CuF_4$, similar to 2D hybrids with Jahn-Teller active ions.[35]

As described above, 1D organic-inorganic hybrids represent quasi one-dimensional systems, because of face-shared $MX_6$ octahedra, forming inorganic chains intercalated by the organic ligands. Example of such a system is a family of Ni-based hybrids.

The $Ni^{2+}$ spins couple antiferromagnetically in inorganic $NiCl_6$-chains[36,37]. Antiferromagnetic (AFM) coupling is common for face-sharing $NiCl_6$ chains[36,38–40]. The direct exchange pathway Ni-Ni introduces an AFM spin interaction which dominates the ferromagnetic interaction, mediated by Ni-Cl-Ni bond angle. These systems represent quasi one-dimensional magnetic spin chains. The in-chain and intra-chain exchange interactions are the subject of discussion of Chapter 6.

## 1.2. Overview of the chapters

### 1.2.1 Multiferroicity

Multiferroics are materials that combine ferromagnetic, ferroelectric, and/or ferroelastic order. Such a combination of properties is of interest for possible spintronics applications. In theory multiferroic material with known magnetoelectric coupling mechanism should provide the possibility to control the magnetic spin with the electric field and vice versa. Another important requirement for the coupling between two orders is the same origin of these phenomena.

Generally, ferroelectricity and (anti-)ferromagnetism rarely coexist in one material. This happens because of the requirement for the magnetism to have atoms with partly-filled d-orbitals, while ferroelectricity demand empty d-orbitals. Therefore, different ways for introduction of the ferroelectricity are of interest, where a remanent polarization is a side effect of magnetism (magnetic spirals) or charge order (charge ordered magnets)[41,42].

As an alternative to these systems the hydrogen-bonds related ferroelectricty appears to be a perfect candidate. Good examples of such a systems are ARS (Ammonium Rochelle Salt)[43,44] and TGS (triglycine sulphate)[45,46]. Organic-inorganic hybrids with perovskite-like structure are of interest[19–22] because some of them show a hydrogen-bonded-related multiferroic behavior[18]. Different mechanisms and contributions were suggested in order to describe the ferroelectric transition in the hybrids[17,18,47].

In Chapter 3 Cu- and Mn-based hybrids are shown to have multiferroic properties. This chapter will mostly discuss the detailed nature of the ferroelectric transition in $CuCl_4(C_6H_5C_2H_4NH3)_2$ and a possible ferroelectric state in the $MnCl_4(C_6H_5C_2H_4NH3)_2$ hybrid. The parameters relevant for the ferroelectric and ferromagnetic phase transitions will be introduced, namely- buckling angle and Jahn-Teller distortion of the $MX_6$ octahedra, will

be introduced. Moreover, in Chapter 4 the relation between these parameters will be shown in order to predict possible magnetoelectric coupling.

### 1.2.2 Tailoring the magnetism in 2D $CuCl_4$-based hybrids

As mentioned in the beginning of the present Chapter, organic-inorganic hybrids adopt structural form of the inorganic part from the perovskite systems. Similar type of structures belong to the family of the layered perovskites, e.g. $K_3Cu_2F_7$[48].

Cu-based hybrid layered hybrids consist of alternating layers of $CuCl_4$ corner sharing octahedra monosheets and ordered organic layers. As will be shown in Chapter 3, organic and inorganic parts of the hybrid share contributions in the multiferroic properties of the compound. In particular ferromagnetism is fully defined by the $CuCl_4$ corner shared octahedra monosheets. Because of Jahn-Teller active $Cu^{2+}$ ions, long and short bonds of the $CuCl_6$ octahedra alternate, resulting in a specific orbital arrangement leading to quasi 3D ferromagnetic ordering.

It is known that for classic rare-earth perovkite systems with collective Jahn-Teller distortion, like $R_{1-x}Ca_xMnO_3$, the size of the R ion does not influence significantly the Jahn-Teller distortion of the octahedra. For the hybrids, the organic ligands play a similar role as the R ion in $R_{1-x}Ca_xMnO_3$. Surprisingly, changing the organic ligand in the $CuCl_4$-based hybrid significantly changes the Jahn-Teller distortion of the $CuCl_6$ octahedra. Therefore, magnetic properties, such as the magnetic transition temperature and single ion anisotropy are different for $CuCl_4$-based hybrids with different organic ligands.

In Chapter 4 magnetic properties and structural dependences of the organic spacers will be discussed. Among others, a linear dependence of the buckling angle on the Jahn-Teller distortion of the octahedra will be presented, providing further insight for the possible magnetoelectric coupling in the compound[5,23].

### 1.2.3 Thin film hybrids

Thin films are the most desirable form of a material for application in devices. Nowadays there are plenty of techniques to grow materials in thin film form. Such methods as Chemical Vapor Deposition[49] (CVD), Pulsed Laser Deposition[32] (PLD) and Molecular Beam Epitaxy[50,51] (MBE) are widely used for solid state compounds and provide reasonable quality films, but require high temperatures and special working conditions. Thin film deposition of the hybrids compounds is, however, challenging due to the different chemical character of the organic and inorganic compounds. One of the main advantages of the hybrids is easy processing due to self-assembly formation. Thus, another set of synthesis techniques is of interest. Besides, the fragile hybrid compounds require gentle methods in order to keep organic network of the compound intact.

In the bulk the $CuCl_4$ layers are coordinated on both sides by the same ligand[5,6,17]. The use of LB implies an alternation of hydrophilic and hydrophobic end groups during the deposition: octadecylamine (ODA) and methylamine (MA) with $CuCl_2$ salt as an inorganic precursor[25,52]. I show that in hybrid thin films the ferromagnetic transition temperature is only slightly reduced in comparison with the bulk despite the Langmuir-Blodgett growth using long alkyl spacers. However, the single ion anisotropy is larger for the Cu-based hybrid films than for the bulk hybrid. Hybrid thin films consist of two phases in which ferromagnetic domains are effectively pinned by an antiferromagnetic second phase, leading to large enhancement of the coercive field.

Structural changes and hybrid formation, imposed by thin film growth are presented in Chapter 5. Moreover, differences in magnetic properties, arising due to the novel deposition technique are discussed, compared to the bulk.

### 1.2.4 Quasi one-dimensional spin chains

The magnetic properties of one-dimensional magnetic systems have been widely studied over the past decades[36,38–40,53–55]. Considerable progress in the understanding of the physics of low-dimensional spin systems was achieved by studying a variety of quasi-one dimensional systems. The well-known example $[N(CH_3)_4]MnCl_3$, TMMC[56,57], represents a S=5/2 antiferromagnetic Heisenberg chain compound with an intrachain exchange constant $J/K_B$=-6,7K. TMMC is one of a large series of compounds with general formula $ABX_3$. Other systems from this family are $CsCuCl_3$[58,59], $CsNiF_3$[60], quasi one-dimensional ferromagnets[61] $[(CH_3)_4N]NiCl_3$ (TMNC)[60], $[(CH_3)_3NH]NiCl_3{*}2H_2O$ (TMAN)[62], and $[C_9H_7NH]NiCl_3{*}3/2H_2O]$[62].

The Ni-based hybrids family represents a one-dimensional class of hybrid compounds. As discussed, in these systems the inorganic backbone is formed by chains of $NiCl_6$ face-sharing octahedra, interconnected by organic molecules. In chapter 6 I will discuss the influence of the organic ligand on the magnetic properties of these compounds.

Interestingly, compounds based on $MnCl_3$ inorganic parts with different organic cations were previously synthesized: $CsMnCl_3$[63,64], $(CH_3NH_3)MnCl_3{*}2H_2O$, $[(CH_3)_2NH_2)]MnCl_3{*}2H_2O$[65]. These systems have same inorganic part- cis$[MnCl_4(OH_2)_2]$ octahedra, which defines the overall magnetic character. The intra-chain magnetic exchange constants remain approximately the same, even though small distortions are present.

However, in Chapter 6 a series of $NiCl_3$-based compounds is presented where the intrachain exchange constant J can be varied by choice of the ligands while keeping the intra- and inter-chain architecture the same. The magnetic properties of the inorganic block can be finely tuned by using different organic moieties. Different organic moieties cause structural modifications, resulting in changes of the intra-chain magnetic interactions. The in-chain nearest neighbor exchange constants *J* can be varied considerably, even though the Ni-Ni distances and Ni-Cl-Ni angles in the

chain are very similar. Moreover, the deviations from the classical 1d magnetic behavior will be discussed.

## 1.3 Conclusions and perspectives

In this thesis layer- and chain-types of organic-inorganic hybrids are discussed. Hybrids exhibit robust magnetic and electronic properties from the inorganic octahedral-formed backbone. Choosing different “building blocks” it is possible to change the structure and properties, correlated to the changes. Also hybrids are easy-processable and structurally flexible due to the self-assembly formation, which is possible because of the hydrogen bonding via the organic part.

Different synthesis techniques were used to synthesize and template these materials in bulk or thin film form. Mostly, the solution growth method was used to synthesize hybrids discussed in the present thesis. This method and important synthesis details are described in Chapter 2.

The dimensionality of hybrids is defined by the metal ion used. The magnetic interactions are dependent on the dimensionality of the inorganic part, which provides the variations of the coupling between the magnetic ions.

In the present thesis, various remarkable properties of the 1D and 2D organic-inorganic hybrids are presented. The dual nature of hybrids makes it possible to combine ferroelectricity and (anti-)ferromagnetism. Furthermore, measurements performed on the CuCl-based hybrids with different organic blocks provide evidence for possible magnetoelectric coupling in the compounds. The use of different organic ligands in 1D hybrids, helps to fine tune the magnetic interaction of the inorganic part. Finally, specific methods to synthesize hybrids as thin films provide the opportunity to synthesize new type of magnetic hybrid thin films with different magnetic anisotropy than in bulk hybrids.

Overall, such a hybrid system gives wide possibilities to create variation of the structure, followed by the corresponding changes of the magnetic and electronic properties of the material.

Importantly, it is shown that the organic blocks have a strong influence on the magnetic and electronic properties, even though structural changes of the inorganic part, implied by the substitution of the organic moiety remain small. In other words, simple selection of the organic moieties for the synthesis can define the specific magnetic or electronic properties of the material. Moreover, such hybrid systems combine properties of different nature like ferroelectricity and magnetism. Further research of the multiferroic properties of such an organic-inorganic hybrids should be focused on the exploration of the magnetoelectric coupling mechanisms predicted by A.Arkenbout and described in this thesis[66].

Recent discovery of the remarkable protovoltaic properties of the Pb-based family of perovskite hybrids opens the new horizons for solar cells research. Possibility to tune properties of hybrids due to the structural flexibility and easy-processing can make a significant contribution to investigate and make possible improvements of the light absorbance properties and understanding of the underlying mechanisms.

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